Kobayashi Laboratory (Special Issue on the Commemoration of the Fortieth Anniversary)

KOBAYASHI LABORATORY (October 1965~)

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This laboratory was established recently to make a specialty of polymer crystallography, however, the actual research project is rather morphology of polymer solids in correlation with their physical properties. As the laboratory is very newly-born, a brief review of its historical background is helpful to characterize the present program of our works.

[1935—1957] Kobayashi started his microscopical study on fibers from 1935 when he joined late Prof. Kita's laboratory of this Institute. Two years later he discovered an important fact that the skin-core structures of rayon fibers were not caused by the rheological behavior of viscose solutions but by the zonal physico-chemical reactions similar to the Liesegang's phenomena.

Joining Horio Laboratory in 1941, Kobayashi planned to utilize an electron microscope for the study of micellar structures lying far beyond the ultimate resolution of optical microscopes, and in close cooperation with Dr. Asao of Toshiba Electric Ltd. he could manage to built an electro-static microscope. In early spring of 1943 world first successful electron photomicrographs of thin cross-sections of viscose fibers were obtained with improved technics for specimen preparation.

While the advantage of the electron microscopy was established, the disadvantage of it for organic specimens became in issue, that is, the change of molecular structures due to the intense dose of electrons. In 1951 our new magnetic electron microscope with an intermediate lens revealed the rapid decay of diffraction patterns even when the thickness of the specimen was thinner than a few hundreds Å.

The indirect method of electron microscopy, such as replica, shadow casting or staining, was a good remedy for this difficulty. Improving these technics, Kobayashi and his coworkers made electron microscopical studies on various processes of fiber materials as follows; the fiber formation of artificial silk (viscose rayon)[1),2),3)] and natural silk[4)], pulping[5)], refining[6)] and paper making[7)]. Similar methods were also applied to the study of synthetic polymers, however, the structural changes by deformation or by heat treatment of those materials had to be examined with a direct method able to reveal the orientation of molecules. Since the organic polymer specimens were readily destroyed by the 50kV electrons, the electron diffractions of limited areas, the best of direct methods, were not always reliable on their results.

As it was assumed that the reduction of inelastic cross-sections of electrons was to secure the molecular arrangements from their rapid destruction during exposure of the specimen to electrons, we started to construct a high voltage electron microscope from the spring of 1954 with special financial aid of the Ministry of Education and technical aid of Shimadzu Seisakusho Ltd.. Toward the end of 1957, the prototype of this 300kV electron microscope together with its high voltage generator of step-up transformers system was accomplished. This was the first practical high

voltage electron microscope which could be utilized for various applied studies[8),9)].

During the trial manufacturing of this powerful instrument, diffraction studies were performed with X-ray. For this purpose an X-ray diffractometer was provided with a stretching device or a heating chamber for the specimen. Dr. Kurokawa, a visiting researcher from Fukui University at that time, succeeded to reveal the changes in long period structures of polyethylene, nylon or other synthetic fibers with diffractometries in small angle regions at various elevated temperatures[10),11)]. While this results were throwing doubt on the popular concept of fringed micellar structure, in September of 1957 a very strange structure was revealed by Kobayashi in the spherulites of polyethylene, that is, the thin lamellar crystals composing spherulites, and more surprising than this was the fact that the long molecular chains were folded in these crystals to arrange their axes perpendicularly to the surfaces of lamellae[12)]. Such structure was incompatible with the proposed model of fringed micellar structure. However, two month later, we found our result in good agreement with that of Dr. Keller of Bristol who had assumed, independently of us, a very similar structure of chain folds in the single crystals of polyethylene.

[1958—1966] The advantage of high voltage electron microscopy had been roughly estimated in consideration of relativistic correction, still the experimental proof remained. According to the theory the inelastic ccross-sections of electrons were to be proportional to β^{-2} [13)]. As the experimental results with this 300 kV microscope showed, the transmissive power of electrons varied with β^2, while the damage to the specimen was reduced almost linearly with the accelerating voltages of electrons[14),15),16),17)]. The latter relationship was very favorable for the microscopy of such electron sensitive materials as polymers. Owing this merit of 300 kV microscope, many interesting observations were performed to reveal the changes in molecular arrangements by the deformation or the heat treatment of the crystalline polymer solids.

Most important results were as follows; 1) The unfolding of folded chains was established as the molecular basis for the "necking" phenomena in the deformation process of spherulitic structure of polymers. 2) The reverse process, namely, the re-folding of extended chains were proved with the stretched and then heat treated specimens[18),19),20)]. We regarded the latter process responsible for the abrupt increase of the long periods in fiber structurs by heating them at the temperatures a little below thier melting points. 3) The deformation process of a spherulite, very complicated as its structure, was clearly analysed with the thorough knowledge about the morphology and mechanical properties of the tublar extruded film of the same polymer. The structure of such film was proved to be one-dimensionally spherulitic, that is, a row structure of lamellar crystals (Keller) or a stacked lamellar structure grown spirally along a preferred direction (Kobayashi)[20),31)].

Since these experiments confirmed the superiority of the high voltage electron microscopy for polymer materials and moreover the relationship of the damage to the accelerating voltage appeared linear up to 300 kV, we tried to construct another high voltage electron microscope with higher accelerating voltage. Taking the increment of β into account, we adopted 500 kV as the most efficient voltage. The fundamental design was very similar to that of the 300 kV microscope[21)], except for the

alterations in high voltage parts such as a Cockcroft-Walton circuit instead of the cascade system and the installation in pressure vessels filled with insulating gas. Shimadzu Seisakusho Ltd. took the trouble again to built this giant microscope with us. The set up of the prototype was finished in the spring of 1964[22], and after the laborious reforms of several weak points (mostly in the accelerator tube) it was installed in a special building at Uji in December 1965[23),24].

The very high stabilities of both accelerating voltage and exciting currents for lenses promised the theoretical resolution of the 500kV microscope to be as high as 1Å, wheeras the actual resolution attained already to reveal 4.5Å spacings of a molecular lattice of the sericite[25]. The voltage dependence of the damage to specimens was measured up to 500kV and the most possible relationship was proportionality with β^{-3}. Why β^{-3} instead of β^{-2} was a interesting problem which would give a key to disclose the vague intermediate processes between the primary acts (ionization of molecules) and the secondary reactions (cross-linking, scission of chains etc.)[26]. Apart from the radiation chemical aspect, the β^{-3} relation assured us of much reduced damage to the specimen at 500kV, therefore it became possible for us to observe directly the lattice images of polymer crystals together with the defects or dislocations in them. As the resolving power is high enough for such purpose, we are now trying the possibility to visualize how the real crystalline states of polymers are.

Nevertheless, we were approaching to this very important point of the polymer crystallography by other indirect means. It had been popularity believed without any positive proof that the surfaces of lamellar crystals were covered with disordered molecular chains as the amorphous regions attaching to fringed micells. In order to examine the real surface structures of lamellae, we employed the epitaxy as the criterion for the regularity of molecular arrangements. Dr. Takahashi succeeded to grow lamellar crystals of polymers epitaxially onto the creaved surfaces of alkali halide single crystals (polyoxymethylene on NaCl and poly-ethyleneoxide on KF)[27]. Those oriented over-growth was realized only when the lattice constants of both overgrown and substrate crystals coincided in two dimensions with misfits of less than 5%. This conditon should be a positive evidence for the surface of lamellar crystals being sharply defined with regular folds of molecular chains. Furthermore we found epitaxies between different polymers and established the epitaxial affinity as an important factor of the cohesions in composite fibers[28] or laminated films[29].

The mechanical properties of polymer crystals were investigated in correlation with their morphology. X-ray diffractometers were the main tools for these studies and the methods or the technics employed were very similar to those for testing metals. The main subjects treated here were as follows; 1) The anisotropy of elastic modulii perpendicular to molecular chain axes[30], 2) The temperature dependence of them compared with the thermal expansions of lattice spacings[30], 3) slips by shear stresses[31], 4) lattice distorsions induced by cross-linking between chains[30], 5) polygonization of crystal with micro-necking[32], 6) modification of crystal lattices under stress, etc.. From those measurements it was pointed out that crystalline polymer solids were very analogous to metals in their mechanical behaviors except for several par-

ticulars due to the long molecular chains. Moreover we could explain the whole plastic deformation processes of crystalline polymer solids with the plastic behaviors of component crystals only[31], that is, without regard to the amorphous regions if existed between crystals[33]. This attempt is revolutional because the amorphous parts in solids were concidered hitherto to be responsible for the plastic deformation of polymers. At this point of view, we are investigating eagerly the nature of the defects or dislocations in polymer crystals[34].

Our most recent work was the measurements of the molecular arrangements during film or fiber formation from polymer melts[35]. It had been long believed that the shear by the drafting forced molten molecules to arrange along the machine direction, yet no experimental evidence had been presented for this view. On the contrary, our results replied in the negative. The orientation of molecules was very poor at the point where the rate of shear was highest, while the orientation increased rapidly at the frost point where the crystallization occurred and the preferential orientation of crystals arose. Therefore the dominant factor of the molecular orientation should be the stacking of the lamellar crystals by their spiral growthes and the promoter of the latter is the screw dislocation. We are surprised by the strange coincidence of the matters treated in our oldest and latest works at the distance of thirty years. Our works are reccuring but advancing as the spiral growth is.

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